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Poster Session HEDM CONFERENCE

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HIGH ENERGY DENSITY MATTER CONTRACTORS CONFERENCE  
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# Measurement of Large Dopant Concentrations by Dopant-Induced Infrared Activity in Solid Parahydrogen

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# High Energy Density Matter (HEDM) Cryosolid Propellants

## HEDM Cryosolid Program Objectives

Trap 5% molar concentration of energetic additives in solid hydrogen.  
Demonstrate size-scalable sample production method.

## Payoffs

### Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$\text{LOX/LH}_2: I_{sp} = 390 \text{ s}$$

$$5\% \text{ B/H}_2 + \text{LOX}: I_{sp} = 500 \text{ s (+30\%)*}$$

$$\text{*calculated for } P_{\text{chamber}} = 1000 \text{ PSIA, } P_{\text{exhaust}} = 14.7 \text{ PSIA}$$

### Greater Propellant Density

$$\text{liquid H}_2: = 0.070 \text{ g/cm}^3$$

$$\text{solid H}_2: = 0.087 \text{ g/cm}^3 (+25\%)$$

$$50/50 \text{ liquid He/solid H}_2: = 0.105 \text{ g/cm}^3 (+50\%)$$

## TASK OBJECTIVE

Develop a technique for quantifying dopant species identities and concentrations in optically dense samples using the dopant-induced infrared (IR) absorptions.

## BACKGROUND

Have demonstrated we can produce gram scale samples of solid  $\text{pH}_2$  doped with HEDM species with concentrations of 0.01 to 0.1%.

Dopants were produced using laser ablation which is not a suitable method for producing high concentrations.

Three teams in the Cryosolids Working Group tasked with: 1) developing new dopant sources; 2) developing a diagnostic for characterizing the new sources; and 3) **developing diagnostic tools for detecting the products of these new sources in  $\text{pH}_2$ .**

## APPROACH

Direct absorption measurements of thick, heavily concentrated samples of HEDM doped  $\text{pH}_2$  solids will not work as a diagnostic for these new sources.

Alternative is to use the dopant-induced IR absorptions as a diagnostic.

## Beer's Law

$$A(\tilde{\nu}) \equiv 2.303 \log_{10} \left( \frac{I_0}{I} \right) = \alpha c l$$

$$c = \frac{A(\tilde{\nu})}{\alpha l} \Rightarrow \frac{2.303 \int_{band} \log_{10} \left( \frac{I_0}{I} \right) d\tilde{\nu}}{l \int_{band} \alpha(\tilde{\nu}) d\tilde{\nu}}$$

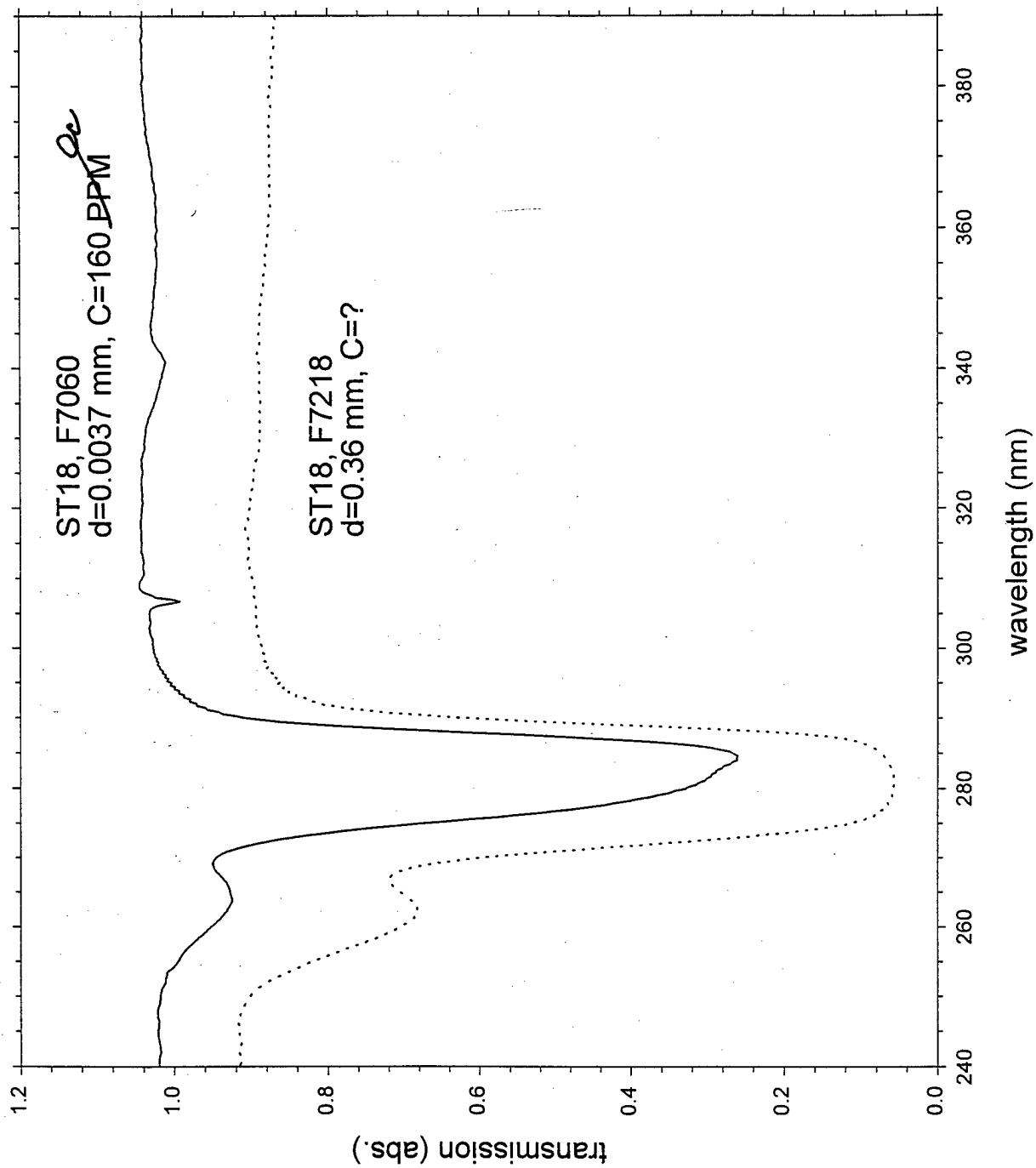
Increased path lengths or highly concentrated samples can cause saturation of the absorption.

If we want to work with gram scale, heavily-doped  $\text{pH}_2$  samples, we require a spectral feature that has a very small intrinsic absorption coefficient ( $\alpha$ ) to compensate for the higher  $c$  and  $l$ .

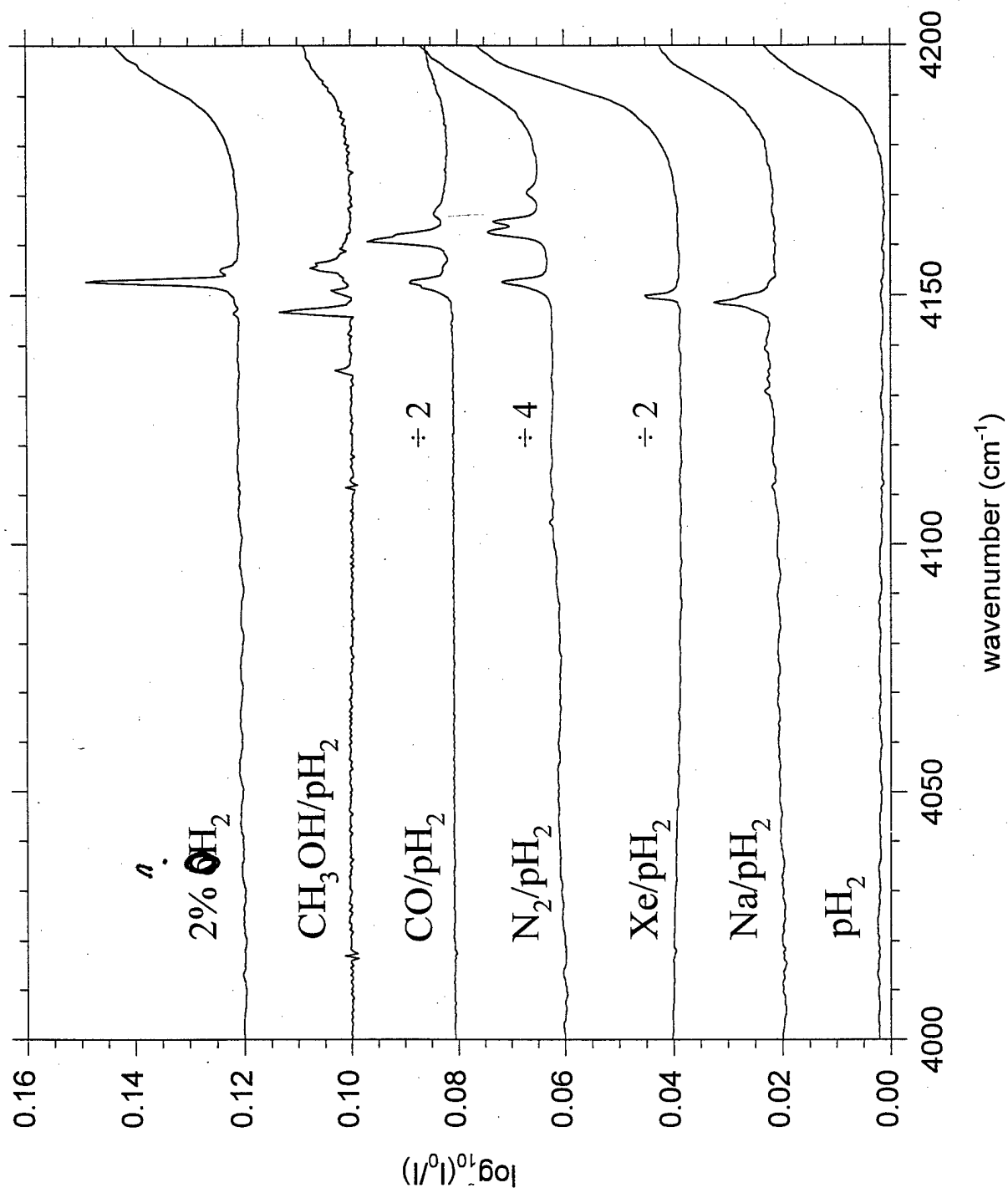
We can use dopant-induced infrared absorptions to determine the concentration.

BUT: Need to determine  $\alpha_{i,\text{ind}} \equiv$  the dopant-host intrinsic absorption strength

# Mg/pH<sub>2</sub> and Mg/oD<sub>2</sub>, T=2K

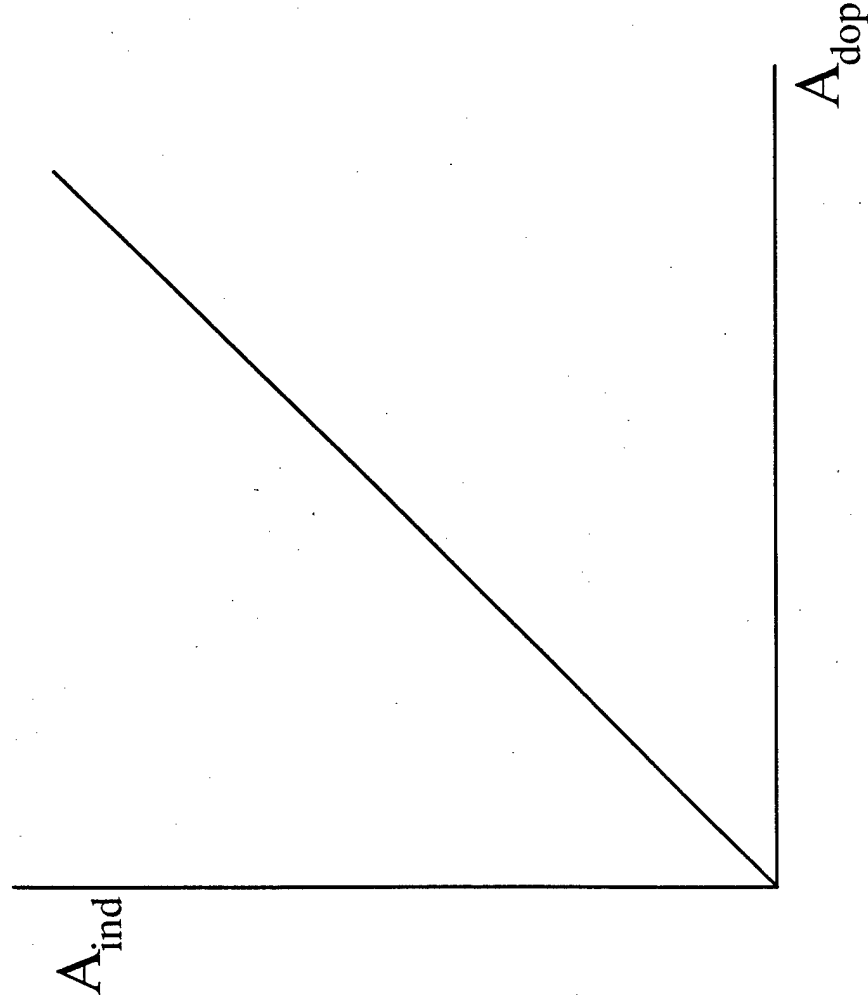


# Examples of Dopant Induced H<sub>2</sub> Absorptions





### Determining $\alpha_{\text{ind}}$ from $\alpha$



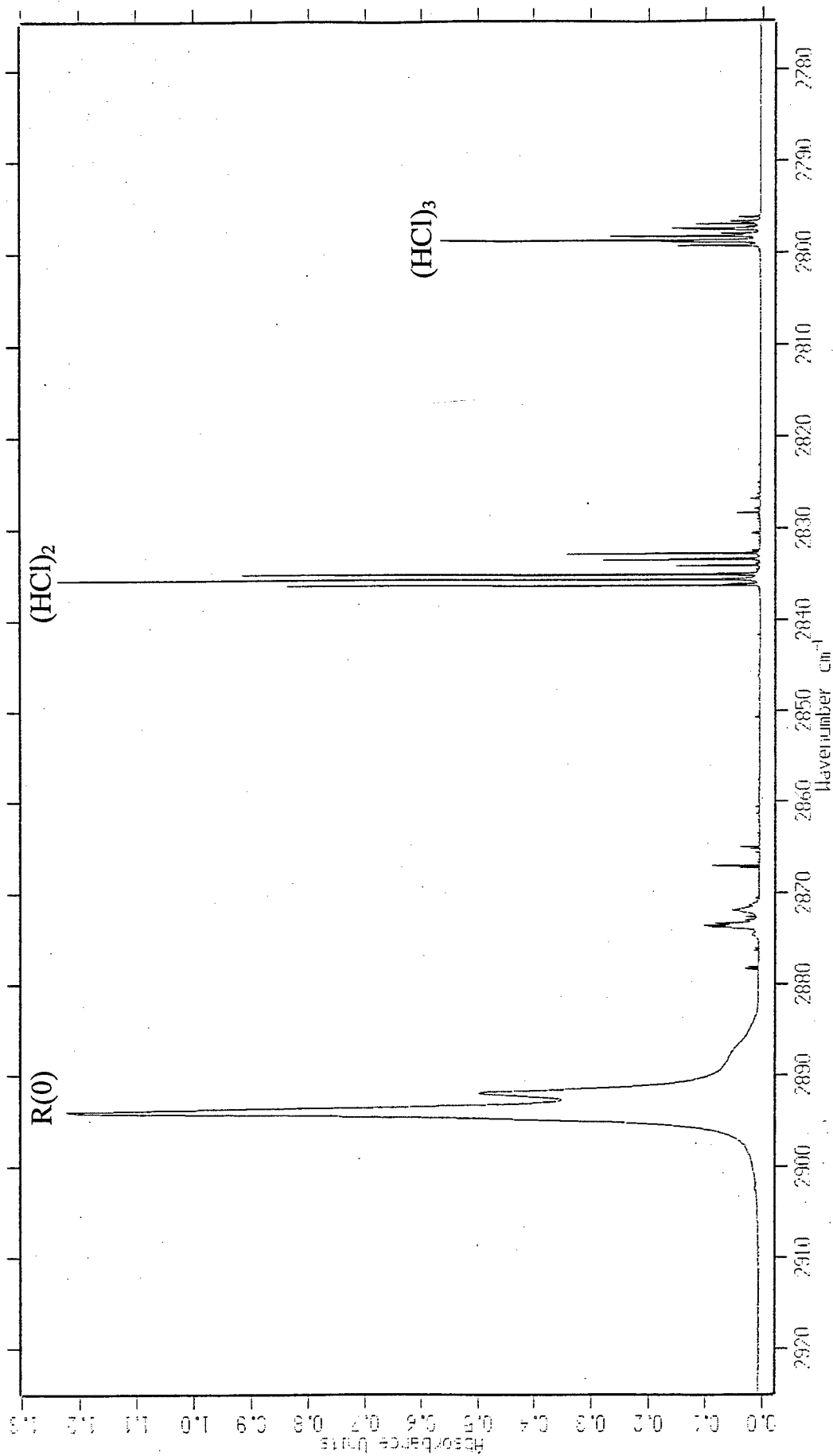
Where:

$$\text{Slope of the line} = \frac{\alpha_{\text{ind}}}{\alpha}$$

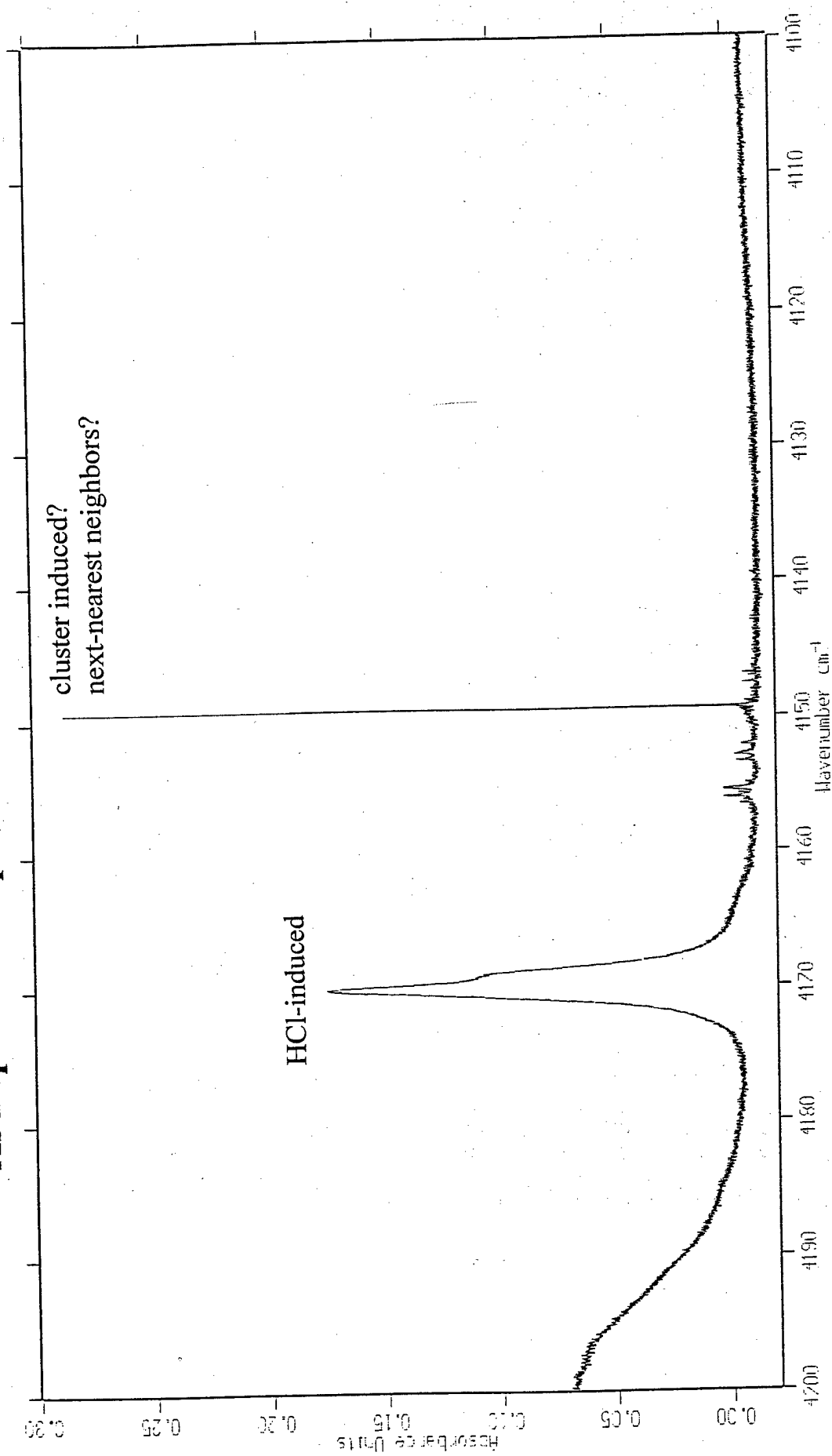
$\alpha \equiv$  property of the dopant in the gas phase

$\alpha_{\text{ind}} \equiv$  property of the dopant and  $\text{pH}_2$  in solid  $\text{pH}_2$

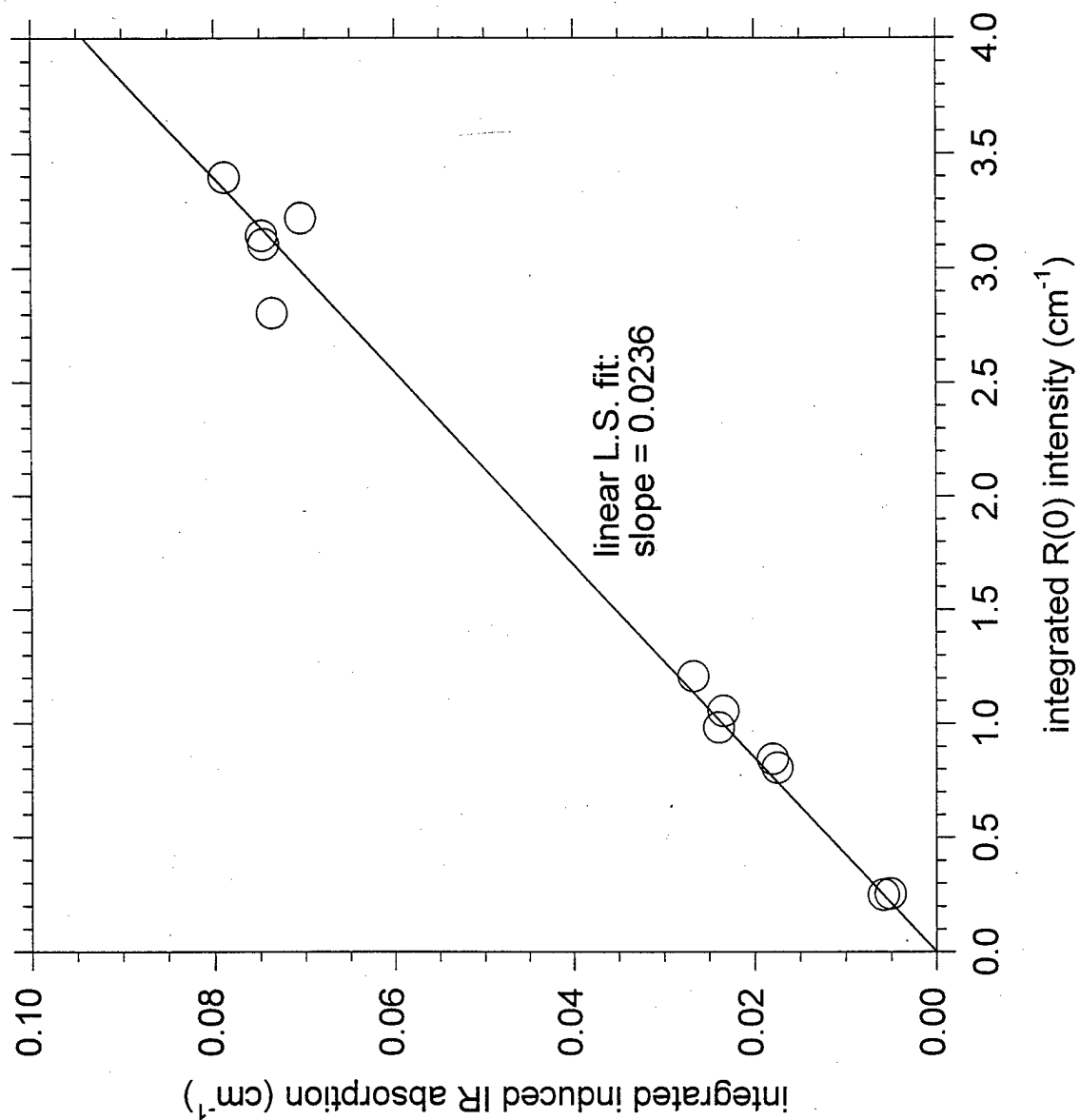
**HCl/pH<sub>2</sub> at 2.4 K, 88 ppm, Resolution = 0.0075 cm<sup>-1</sup>  
Annealed Sample, HCl Absorptions Region**



**HCl/pH<sub>2</sub> at 2.4 K, 494 ppm, Resolution = 0.0075 cm<sup>-1</sup>  
As Deposited Sample, Induced Absorption Region**



# Correlation between HCl-Induced $\text{pH}_2$ IR Absorption and HCl $R(0)$ Absorption



### HCl-Induced pH<sub>2</sub> Intrinsic IR Absorption Strength

$$\int \alpha_{\text{ind}}(\text{HCl}/\text{pH}_2) dv = 0.0236 \int \alpha(\text{HCl}) dv$$

literature:  $\int \alpha(\text{HCl}) dv = 32 \text{ km/mol}$

$$\therefore \int \alpha_{\text{ind}}(\text{HCl}/\text{pH}_2) dv = \underline{\mathbf{0.75 \text{ km/mol}}}$$

**Question:** What is the maximum, measurable concentration of HCl/pH<sub>2</sub>?

Assume: a) 1 mm thick sample

b)  $\int A_{\text{max}} dv = 2 \text{ cm}^{-1}$

$$c_{\text{max}} = \frac{2.303 (2 \text{ cm}^{-1})}{(0.1 \text{ cm})(7.5 \times 10^{-4} \frac{\text{cm}}{\text{mol}})}$$

**Answer:**

$$= 6.2 \times 10^{-4} \text{ mol/cm}^3$$

$$\Rightarrow 1.4\% \text{ HCl}/\text{pH}_2$$

## **SUMMARY**

For millimeters thick, heavily-doped samples, direct absorption spectroscopy fails because of limitations on dynamic range and achievable signal-to-noise levels.

Dopant-induced  $\text{pH}_2$  transitions are a possible solution to this problem.

- 1) appear to obey Beer's Law
- 2) are very weak IR transitions (i.e., increased dynamic range for heavily doped samples)

For HCl in  $\text{pH}_2$ , the intrinsic absorption strength is approximately 2.4% of the intrinsic absorption strength of HCl in the gas phase.

Can calculate the maximum measurable concentration for a HCl-doped  $\text{pH}_2$  solid: 1.4% for a 1-mm thick sample, achieving objective of measuring  $\sim 1\%$  concentration in millimeters thick samples.

## **FUTURE DIRECTIONS**

We are in the process of completing a survey of various dopants in solid  $\text{pH}_2$  to determine the generality of using the induced absorptions for concentration measurements.